International Journal of Mass Spectrometry 408 (2016) 33–37

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

Young Scientist Feature

The different cones combination enhanced sensitivity on MC-ICP-MS: The results from boron isotope analysis

He Maoyong[a,d,*], Jin Zhangdong[a], Lu Hai[b], Deng Li[a], Luo Chongguang[c]

[a] State Key Laboratory of Loess and Quaternary Geology, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an 710061, China
[b] Division of Chemical Metrology & Analytical Science, National Institute of Metrology, Beijing 10013, China
[c] State Key Laboratory of Ore Deposit Geochemistry, Institute of Geochemistry, Chinese Academy of Sciences, Guiyang 550002, China
[d] Shaanxi Provincial Key Laboratory of Accelerator Mass Spectrometry Technology and Application, Xi'an 710061, China

ARTICLE INFO

Article history:
Received 6 May 2016
Received in revised form 23 August 2016
Accepted 30 August 2016
Available online 3 September 2016

Keywords:
Cone
Multi-collector inductively coupled plasma mass spectrometer (MC-ICP-MS)
Sensitivity
Boron isotope

ABSTRACT

The sensitivity of multi-collector inductively coupled plasma mass spectrometers (MC-ICP-MS) can be significantly improved using different sample and skimmer cones with different orifice diameters and angles. In this study, an MC-ICP-MS with three typical combinations of sample and skimmer cones [(H skimmer cone + standard sample cone (Standard + H), X skimmer cone + standard sample cone (Standard + X) and X skimmer cone + Jet sample cone (Jet + X)] was used to measure the boron isotopes, and the effect of the different combinations of sample and skimmer cones on the sensitivity of the MC-ICP-MS and the underlying physical principles were investigated. The results suggest that more ions can be introduced into sample cones with larger orifices, which results in increased sensitivity. Compared with standard skimmer cones (which have cylindrical entrances and trumpet-shaped exits), X skimmer cones (which have trumpet-shaped entrances and exits) can provide more space for ion beams to entrance the skimmer's orifice after they are subjected to the space-charge effect.

1. Introduction

As testing techniques develop, and especially since the use of multi-collector inductively coupled plasma mass spectrometers (MC-ICP-MS) in the study of geochemistry began in the 1990s, the evolution of non-traditional transition metal isotopes has been successfully tracked, which has led to the rapid development of the stable isotopic geochemistry of transition metals, which is on the cutting edge of research in earth science [1,2].

The interface is the heart of an MC-ICP-MS; the sampler and skimmer cones are its key parts. They can efficiently transport plasma ions into the mass spectrometer. The two sides of the cones are completely different: one side is corroded and kept at a normal pressure and a high temperature, and the other side is clean and kept in a vacuum at a constant temperature. Their purpose is to continuously and homogeneously transport the ions generated by high-pressure argon plasma in the atmosphere into the vacuum part of the mass spectrometer for mass separation and analysis. Therefore, the transport performance can directly affect the analytical properties of the instrument [3]. The actual performance of an ICP-MS/MC-ICP-MS is strongly affected by physical characteristics of the sample and skimmer cones, such as the cone geometry design, pore size, inside and outside cone angles, and both size and materials. Moreover, the performance is also influence by instrument sensitivity, signal stability, both polyatomic and doubly charged ion yields, and discrimination quality. Therefore, studies on cones have attracted mass designers and engineers.

The Neptune Plus MC-ICP-MS (Thermo Fisher Scientific, Germany) is a new-generation instrument for isotopic analysis that is equipped with a dry pump that functions at a high rate (100 m^3/h). In addition, the sample and skimmer cones have been upgraded to a Jet sample cone and a high-performance X skimmer cone to improve the instrument's sensitivity. In previous studies, the sensitivity, accuracy, and precision of different isotopic systems were investigated with various combinations of sample and skimmer cones [4–14]. It can be concluded that (1) the sample cone's sensitivity can be increased five to ten times by combining a Jet sample cone with a high-performance X skimmer cone, and (2) the sensitivity enhancement varies for isotopes of different elements when a Jet sample cone and an X skimmer cone are used. When testing strontium, neodymium, hafnium, lead, and uranium isotope ratios, the highest sensitivity can be obtained by combining a Jet sampler cone with an X skimmer cone (Jet + X), and when

* Corresponding author at: State Key Laboratory of Loess and Quaternary Geology, Institute of Earth Environment, Chinese Academy of Sciences, Xi'an 710061, China.
E-mail address: hemy@ieecas.cn (M. He).

http://dx.doi.org/10.1016/j.ijms.2016.08.010
1387-3806/

testing lithium and magnesium isotope ratios, the highest sensitivity can be obtained by combining a standard sample cone with an X skimmer cone (Standard + X) [6]. Therefore, the instrument's sensitivity can be improved by using different combinations of cones, i.e., using with a Jet or an X cone to reduce the consumption of the sample and extend the application of the MC-ICP-MS to broader fields. However, the sensitivity enhancement has only been studied by comparing a standard sample cone and a Jet sampler cone. The major reason for this is that the cone's orifice is increased from 0.8 mm to 1.2 mm to enlarge the ion beam input into the spectrometer. According to this comparison, the improvement in the sensitivity is due to the difference in the cone angle. These explanations are not convincing unless they include a discussion of the sensitivity enhancement that results from different cone combinations. Many MC-ICP-MS operators still do not fully understand why varying combination of cones may improve the sensitivity, whether the sensitivity can be continuously improved by using a sample cone with a larger diameter, or whether the sensitivity can be further enhanced by modifying the current cones. To address these issues in the present study, boron isotopes were selected as representative subjects for comprehensively studying the sensitivity enhancement of an MC-ICP-MS with three different cone combinations (H skimmer cone + standard sample cone (Standard + H), X skimmer cone + standard sample cone (Standard + X) and X skimmer cone + Jet sample cone (Jet + X)) and the underlying physical principle. There are the same characteristics when measured lithium and magnesium isotopes. This study can provide a basic principle for the use of MC-ICP-MS operators.

2. Experimental

2.1. Instrumentation and reagents

Isotopic measurements were conducted on a NEPTUNE Plus MC-ICP-MS (Thermo Fisher Scientific, Germany) at the State Key Laboratory of Loess and Quaternary Geology, Institute of Earth Environment in Xi'an, Chinese Academy of Sciences (IEECAS). This instrument is a double-focusing magnetic sector instrument with variable dispersion (17%) ion optics. Nine Faraday cups are installed on the instrument; eight are on two sides of the center cup.

The standard material for the B isotope analysis, NBS951, was obtained from the National Institute of Standard and Technology (NIST, 100 Bureau Dr., Gaithersburg, MD 20899, USA). The H_2O used in the experiment was purified with a Milli-Q system at a resistance of 18.2 MΩ. The HNO_3 used in the experiment was purified with a DST-1000 sub-boiling distillation device (Savillex Co., 10321 West 70th Street Eden Prairie, MN 55344-3446, USA).

2.2. B isotope measurement

All isotope measurements were carried out on a MC-ICP-MS, which enables a static measurement of m/z 10 and m/z 11 on Faraday cups [10,15,16]. The optimum instrument parameters were obtained using 45 ng/g NIST SRM 951 standard solution. The operating parameters are given in Table 1.

3. Results and discussion

3.1. Sensitivity of different cone combinations

The memory effect is significant during the measurement of boron isotopes using MC-ICP-MS. To reduce the rinse time between the different samples, a 45 ng/g NIST SRM 951 standard solution was used as a tuning solution. The intensity of ^{11}B ion beam for three cone combinations are shown in Fig. 1. In this study, the ^{11}B signal was enhanced by approximately factors of 2 and 4 with for combinations with the X skimmer cone and the Jet sample cone, respectively, compared to, that of using standard cones.

Table 1
Typical operating parameters for B isotopes measurement on Neptune MC-ICP-MS.

Parameter	Value
RF forward power	1250 W
Ar cooling gas	16 L min^{-1}
Ar auxiliary gas	0.7–0.9 L min^{-1}
Ar sample gas	0.8–1.15 L min^{-1}
Extraction voltage	2000 V
Acceleration voltage	10 kV
Detection system	L3, H3 Faraday cups
Nebulizer	Low-flow PFA microcentric (50 μL min^{-1})
Spray chamber	47 mm PFA spray chamber
Uptake time	90 s
Number of cycles	20
Integration time	4.194 s
Measurement time	4 min
Rinse time	20 min

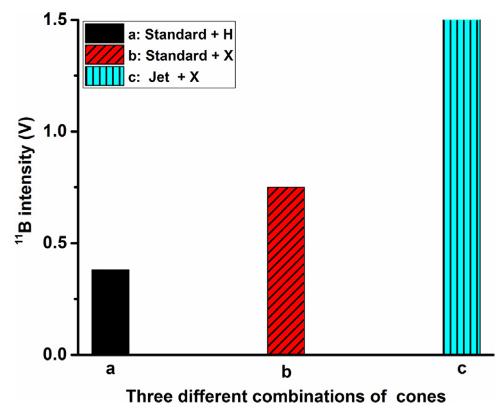

Fig. 1. The integrated average signal intensity of ^{11}B from B standard (NBS 951) using three different sample and skimmer cone combinations. a: standard sample cone + H skimmer cone (Standard + H); b: standard sample cone + X skimmer cone (Standard + X); c: Jet sample cone + X skimmer cone (Jet + X).

3.2. The principle of sample cone sensitivity

The sample cone and the skimmer cone are mainly part of interface of an ICP-MS/MC-ICP-MS. Therefore, a well-designed cone interface can improve the instrument's properties, increase the signal sensitivity, and reduce background noise.The sample cone extracts the carrier gas (ions, neutrons, and electrons in random motion) from the central plasma path through the cone's orifice and into the first-stage vacuum chamber. The ions, neutrons, and electrons extracted by the post-cone vacuum rapidly expand and form a supersonic jet. The main difference between a Jet sampler cone and a regular sampler cone is the orifice's diameter. The orifice diameter of a regular sampler cone is 0.8 mm and that of a Jet sampler cone is 1.2 mm (Fig. 2). As shown in Fig. 2, the larger the diameter of the sample cone's orifice is, the larger the size of the sample cone's orifice is, which allows a larger number of ions enter the sample cone and enhances the spectrometer's sensitivity. The extraction efficiency of an ICP-MS is largely affected by geometry of sampling cone. The gas density, speed and vacuum retention of the transport plasma ions affect overall system performance. Therefore, the kinetics of plasma stream after sample cone has profound importance for significance to improving the sensitivity, and stability of instrument.

According to previous studies, the motion of a plasma through the sampler cone is similar to the process of a low-density flow in a wind tunnel proposed by Ashkenas [16]. Consequently, the Com-

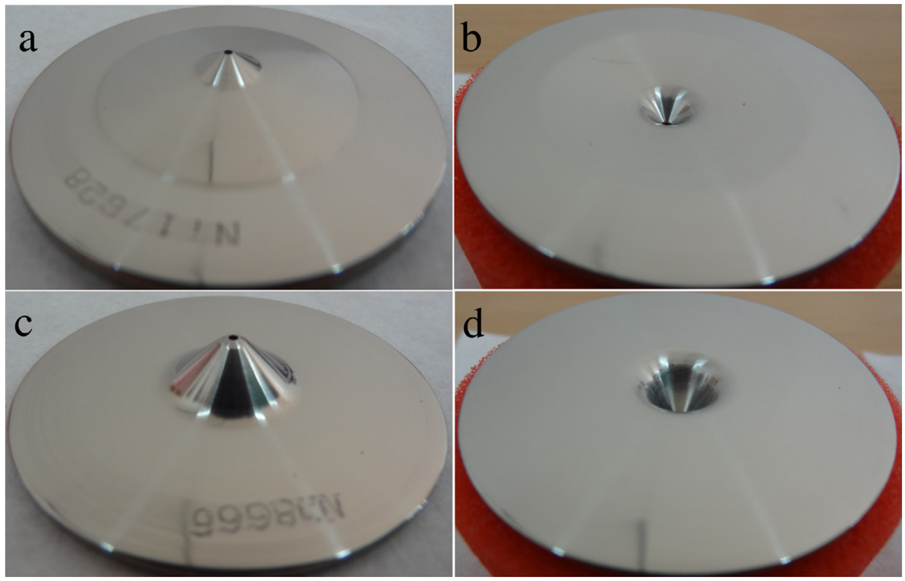

Fig. 2. The different between sample cones from photo. a and b: the front and back sides of standard sample cone; c and d: the front and back side of Jet sample cone.

putational Fluid Dynamic (CFD) is used to describe the movement of plasma ions. The equation for the ion beam (G_0) passing through the sampler cone is [17]

$$G_0(\text{atoms s}^{-1}) = 0.445 n_0 a_0 D_0{}^2, \qquad (1)$$

where n_0 is the density of ions at the source, a_0 is the local speed of sound, $a_0 = D_0(rKT_0/m)^{1/2}$, $r = C_p/C_v$, and D_0 is the diameter of the sampler cone's orifice. K is the Stefan-Boltzmann constant, and m is the mass of an argon atom.

Regarding the lens system, the value of T_0 is 5000 K. In the calculation of G_0 (Eq. (1)), the minimum orifice diameter that ensures the extraction of a certain number of plasma ions is 0.8 mm. The diameter of the sampler cone's orifice not only must be greater than the minimum value but also should not exceed a certain value because an orifice if it is too large can draw more plasma ions (wanted) and air (unwanted) into the instrument. To avoid the unnecessary extraction of air, a vacuum pump with a relatively high pumping rate is required.

At one atmospheric pressure, the flow of the neutrons, electrons, and ions generated in the plasma can rapidly expand to form a supersonic jet after being extracted by the pressure difference caused by the low vacuum after the sampler cone's orifice. The jet zone is composed of a silent zone and a free expansion chamber and is surrounded by a tubular wave and a Mach disk shock wave. The flow that terminates before the Mach disk is stable in the silent zone of the jet, and the torrent after the Mach disk is complex and unstable. Therefore, to obtain the best circumstances during ion extraction, the skimmer cone in the second stage of the interface should be placed in the silent zone where the flow is stable to extract a stable stream ions for analysis. In fact, the best ion transport occurs when sampling is performed at the point in the silent zone that is two-thirds of the way from the sampler cone's orifice to the Mach disk.

The distance between the orifice of the sample cone and the Mach disk can be calculated using the following equation:

$$X_m = 0.67 D_0 (P_0/P_1)^{1/2} \qquad (2)$$

In this equation, X_m is the distance between the orifice of the sample cone and the Mach disk, P_0 is the pressure in the inductively coupled plasma (ICP) source, and P_1 is the background pressure of the expansion chamber. The diameter of the sample orifice, D_0, is 0.8 mm, and because $P_0 = 2.5 \times 10^4$ Pa, the background pressure in the expansion chamber is approximately 150 Pa, which leads to $X_p = 2/3\ X_m$ (X_p is approximately 6 mm). Therefore, the best location for the skimmer cone is $X_p = 6$ mm. In Fig. 3(a), the mass flux at each orifice is calculated using the corresponding orifice diameters. As shown in Fig. 3, when D_0 is increased from 0.8 mm to 1.2 mm, the mass flux at X_m is positively associated with the size of the orifice and reaches its maximum value when D_0 is 1.2 mm. Then, as D_0 is increased from 1.2 mm to 1.3 mm, the mass flux begins to decrease, which indicates that 1.2 mm is the optimal diameter for the sample orifice. Fig. 3(b) reflects changes in the pressure as the diameter of the sample cone's orifice increases for an axial distance, Z, of 8 mm. As the diameter of the sample cone's orifice increases, the post-cone pressure increases from 200 Pa to 350 Pa. As shown in Eq. (1), the post-cone ion density increases with the diameter of the sampler cone's orifice. A larger orifice allows more ions to pass through the sample cone. In addition, as the diameter of the sample cone's orifice increases, the ion flux increases, which implies that the amplification effect of the orifice diameter is greater than its negative effect on the velocity. The post-cone ion density is inversely correlated with the diameter of the sample cone's orifice. A larger sample cone orifice diameter can lead to a higher post-cone pressure and a vacuum that is less sustainable. An oversized orifice can significantly affect the vacuum's sustainability and keep the ion density from reaching an ideal value.

3.3. *The principle of skimmer cone sensitivity*

The skimmer cone's task is to selectively transfer the central portion of the expansive jet from the sampler orifice to the second-stage vacuum chamber. In the extraction lens, electrons are repulsed and positrons are extracted and accelerated; neutrons continue in a straight line without being affected by the electric field. The ICP ion source ionizes the sample. All of the ions are injected from a plasma torch carried by the argon flow and partially extracted at the interface, where they are converted into an ion beam. The plasma is quasi-neutral in the first-stage vacuum, until it reaches the orifice of the skimmer cone. This status is changed during the second expansion of the rarefied ion beam, which occurs after it passes through the skimmer cone. Behind the sampler cone is the expansion chamber, which has a reduced pressure of 300 Pa. Within 1 cm after passing through the sampler cone, the thermal energy of the plasma (5000–7500 K) is converted into kinetic

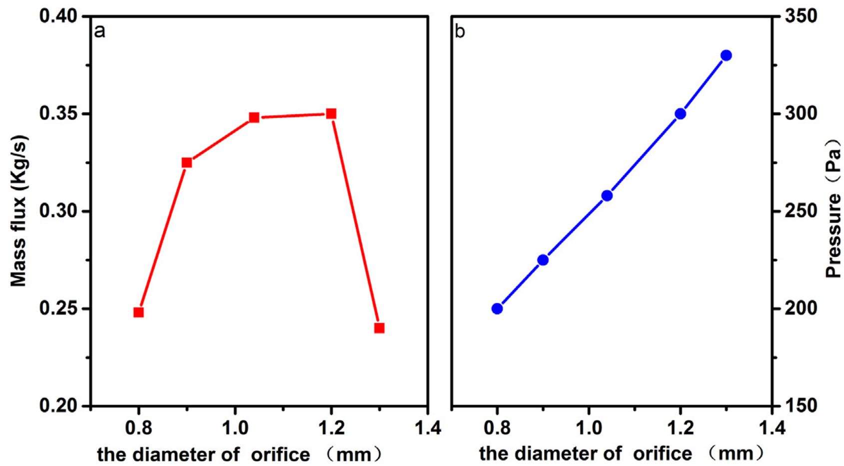

Fig. 3. The relationship between cone diameter and (a) mass flux and pressure.

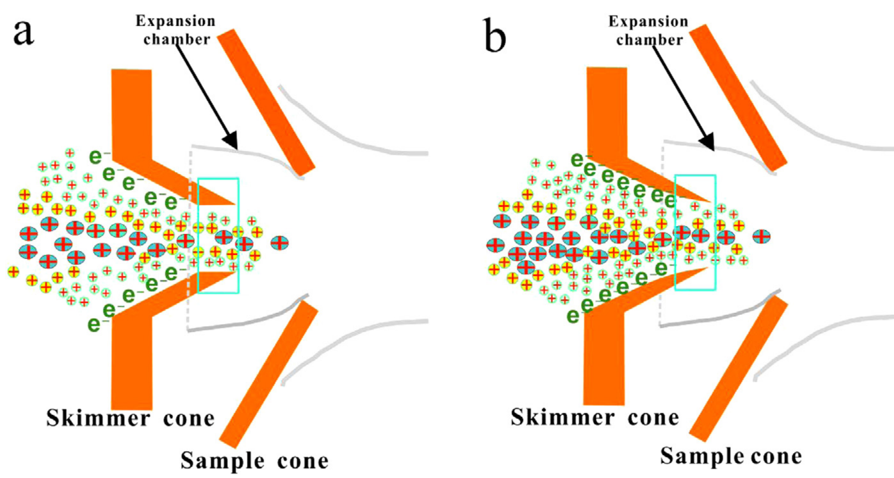

Fig. 4. The space-charge effect behind skimmer cone.

energy (100–200 K), and the gas's expansion speed (~2500 m/s) surpasses the speed of sound. Although the electron temperature remains nearly constant (5000–7500 K), the electron density is considerably reduced within 5 μm because most of the electrons are separated from the ions. Behind the skimmer cone is the intermediate chamber, which has a reduced pressure of 10^{-3} Pa. Along the inner well of the skimmer cone, the negative ion beam is radially distributed, and the positive ion beam is distributed in the axial direction. The positive charges repel each other in this restricted space, which creates the space-charge effect.

As shown in Fig. 4, behind the skimmer cone, the repulsion of the positive charges diffuses the ion beam; the positive ions with more mass and higher kinetic energy are concentrated in the central area of the ion beam, and the ones with less mass and lower kinetic energy are repelled to the far edge. The nickel X skimmer cone and the regular nickel skimmer cone both have orifices that are 0.8 mm in diameter; the main difference is their dip angles. The regular nickel skimmer cone, shown in Fig. 4(a), has a cylindrical entrance and a trumpet-shaped exit; the ion beam first moves in a narrow cylindrical tube and then, expands around the trumpet-shaped orifice. In contrast, Fig. 4(b) shows the structure of the nickel X skimmer cone. Unlike the regular nickel skimmer cone, the X skimmer cone has a completely trumpet-shaped form, which results in a different space-charge effect. Compared with the regular cone, the trumpet-shaped X skimmer cone provides more space in which the ion beam is impacted by the space-charge effect. Consequently, more of the ion beam can be input to the interface, which introduces more ions into the mass spectrometer and thus improves the instrument's sensitivity.

4. Conclusion

Using an MC-ICP-MS with three typical combinations of sample and skimmer cones (Standard + H, Standard + X and Jet + X), instrument sensitivity improved and the physical mechanism involved were discussed. The results of the experiments indicated the following:

(1) More ions can be introduced into sample cones with larger orifices, which results in increased sensitivity; the optimal sample orifice diameter is 1.2 mm based on the calculation. Based upon theoretical calculation, a diameter of 1.2 mm for the is maximum tapered mouth of the sampling cone is identified.
(2) Compared with standard nickel skimmer cones (which have cylindrical entrances and trumpet-shaped exits), X skimmer cones (which have trumpet-shaped entrances and exits) can provide more space for ion beams to exit the skimmer's orifice after being subjected to the space-charge effect. Consequently, the number of ions input into the mass spectrometer is increased and improves its sensitivity.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (Nos. 41573013 and U1407109), Key Program of the West Light Foundation of Chinese Academy of Sciences (29Y42904101), Natural Science Fund of Shaanxi Province (2015JM4143) and The Academic Frontier Project of State Key Laboratory of Ore Deposit Geochemistry.

References

[1] L. Yang, Mass Spectrom. Rev. 28 (2009) 990–1011.
[2] J.S. Becker, Inorganic Mass Spectrometry: Principles and Applications, John Wiley and Sons, Chichester, 2007, pp. 29.
[3] N. Shirai, M. Humayun, J. Anal. At. Spectrom. 26 (2011) 1414–1420.
[4] Y. Nishio, K. Okamura, M. Tanimizu, T. Ishikawa, Y. Sano, Earth Planet. Sci. Lett. 297 (2010) 567–576.
[5] Z.C. Hu, Y.S. Liu, W.G. Liu, W. Zhang, X.R. Tong, L. Lin, K.Q. Zong, M. Li, H.H. Chen, L. Zhou, L. Yang, J. Anal. At. Spectrom. 27 (2012) 1391–1399.
[6] K. Newman, J. Anal. At. Spectrom. 27 (2012) 63–70.
[7] J.L. Fu, Z.C. Hu, W. Zhang, L. Yang, Y.S. Liu, M. Li, K.Q. Zong, S. Gao, S.H. Hu, Anal. Chim. Acta 911 (2016) 14–26.
[8] B. Gueguen, O. Rouxel, E. Ponzevera, A. Bekker, Y. Fouquet, Geostand. Geoanal. Res. 37 (2013) 297–317.
[9] L. Lin, Z.C. Hu, L. Yang, W. Zhang, Y.S. Liu, S. Gao, S.H. Hu, Chem. Geol. 386 (2014) 22–30.
[10] M. Schiller, E.V. Kooten, J.C. Holst, M.B. Olsen, M. Bizzarro, J. Anal. At. Spectrom. 29 (2014) 1406–1416.
[11] S.A. Liu, D.D. Li, S.G. Li, F.Z. Teng, S. Ke, Y.S. He, Y.H. Lu, J. Anal. At. Spectrom. 29 (2014) 122–133.
[12] V. Balter, N. Vigier, Metallomics 6 (2014) 582–586.
[13] X.Y. Nan, F. Wu, Z.F. Zhang, Z.F. Hou, F. Huang, H.M. Yu, J. Anal. At. Spectrom. 30 (2015) 2307–2315.
[14] M.Y. He, Y.K. Xiao, Z.D. Jin, Y.Q. Ma, J. Xiao, Y.L. Zhang, C.G. Luo, F. Zhang, Anal. Chem. 85 (2013) 6248.
[15] M.Y. He, Z.D. Jin, H. Lu, T.X. Ren, Anal. Methods 7 (2015) 10322–10327.
[16] H. Ashkenas, F. Sherman, Rarefied Gas Dyn. (1966) 84–105.
[17] C.Q. Sun, X.H. Zhao, Y. Wang, Chin. J. Vac. Sci. Technol. 32 (2012) 928–932.